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PATENT SPECIFICATION

NO DRAWINGS

Inventor: JOSEPH OLDHAM

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Int. Cl.:—C 08 g 19/00

COMPLETE SPECIFICATION

Polyamides

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polyamide condensates and particularly to polyamide condensates suitable for forming elastic shaped articles such as filaments.

The invention provides condensation products of a dicarboxylic acid with a mixture of a diaminopolyalkyleneoxy compound and an aliphatic, cycloaliphatic or alkyl cycloaliphatic amino acid and/or lactam, and optionally an aliphatic, cycloaliphatic or aromatic diamine.

Instead of a single dicarboxylic acid, diaminopolyalkyleneoxy compound, amino acid or lactam, or diamine mixtures of the said compounds may be used.

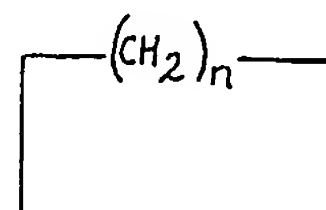
As dicarboxylic acids we prefer in particular aliphatic dicarboxylic acids of the formula—



in which n represents zero or a positive integer from 1 to 10. Adipic acid is particularly suitable. Other suitable aliphatic dicarboxylic acids include oxalic acid, succinic acid, glutaric acid, sebacic acid and dodecanedioic acid.

Other suitable dicarboxylic acids are cycloaliphatic, alkylcycloaliphatic, aromatic and alkyl aromatic dicarboxylic acids. By cycloaliphatic dicarboxylic acids we mean acids containing an alkylene ring structure represented by the formula:—

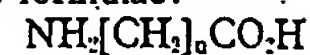
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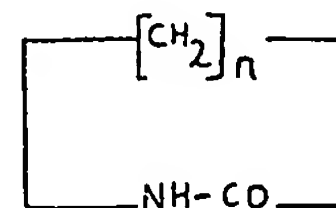
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wherein n is from 5 to 16, two hydrogen atoms not on the same or adjacent carbon atoms being replaced by two carboxy groups to form the corresponding dicarboxylic acids. If aromatic acids are used the carboxylic groups should not lie on adjacent carbon atoms of a ring system. Examples of such dicarboxylic acids include hexahydroterephthalic acid, hexahydro - p - xylylene - α, α' - dicarboxylic acid, p - xylylene - α, α' - dicarboxylic acid, terephthalic acid and isophthalic acid.

By aliphatic amino acids or lactams we mean in particular ω -amino aliphatic carboxylic acids and the derived lactams. Particular compounds of this class may be represented by one of the formulae:—



or

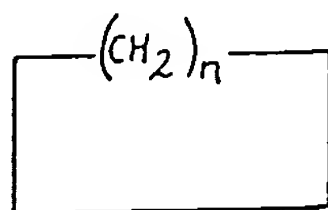


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in which is is a n in which n is a positive integer from 2 to 11. Caprolactam is particularly suitable. Other suitable lactams include laurino-lactam(dodecanolactam), enantholactam and capryllactam. By cycloaliphatic amino acids we mean

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amino acids containing an alkylene ring structure represented by the formula:—

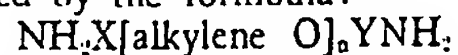


where n is from 5 to 16, two hydrogen atoms not on the same or adjacent carbon atoms being replaced by an amino and a carboxyl group respectively.

In alkyl cycloaliphatic amino acids the amino and carboxyl groups can be attached to the ring or to side chain carbon atoms.

Examples of cycloaliphatic and alkyl cycloaliphatic amino acids include 4 - aminocyclohexanecarboxylic acid, 4 - aminomethyl - cyclohexanecarboxylic acid and 4 - aminocyclohexylacetic acid.

By a diaminopolyalkyleneoxy compound we mean a linear compound containing two terminal amino groups joined directly or through suitable linking groups to a polyalkyleneoxy chain. Such compounds may conveniently be represented by the formula:—



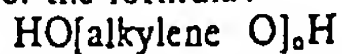
in which X represents a direct link or linking group, Y represents a linking group and n is a positive integer. The alkylene groups in any one polyalkyleneoxy chain may be all the same or the chain may contain more than one kind of alkylene group, for example it may contain a mixture of ethylene and propylene groups. The alkylene groups may contain from 2 to 12 carbon atoms and carry substituents such as alkyl groups. Such diaminopolyalkyleneoxy compounds may be obtained, for example, from a polyalkyleneoxy diol of the formula:—



by conversion of the hydroxyl groups into halogen atoms, for example into chlorine atoms by reaction with thionyl chloride, followed by reaction of the resulting dihalogeno compound with ammonia to give the corresponding diamino compound; in which case X represents a direct link and Y represents an alkylene group. Alternatively they may be obtained from a polyalkyleneoxydiol of the formula:—



by reaction with acrylonitrile to give the bis - β - cyanoethyl ether followed by reduction to the corresponding bis - γ - aminopropyl ether; in which case X represents the group $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ and Y represents the group $-\text{CH}_2\text{CH}_2\text{CH}_2-$. Alternatively again they may be obtained from a polyalkyleneoxydiol of the formula:—



by reacting with a 2 - aminomethyl - 3,4 - dihydro - 2H - pyran as described in Specification No. 1,087,335; in which case X represents a 2 - methylene tetrahydropyran - 6 -

oxy group and Y represents a 2 - methylene-tetrahydropyran - 6 - yl group.

The diaminopolyalkyleneoxy compounds also include those diamines which may be prepared in known manner from alkylene oxide condensates containing two hydroxyl groups. Such alkylene oxide condensates may be obtained by reacting an alkylene oxide or a mixture of alkylene oxides with a compound containing two hydrogen atoms reactive with the alkylene oxide, for example water, a diol, a dihydric phenol, a dicarboxylic acid, a primary amine, a primary amide or a bis-secondary amine. Such alkylene oxide condensates includes:—

(1) alkylene oxide condensates of glycols, especially of glycols containing more than 4 carbon atoms, for example 1,6 - hexanediol,

(2) alkylene oxide condensates of primary amines for example methylamine, ethylamine and hexadecylamine, and

(3) alkylene oxide condensates of dihydric phenols, for example, diphenylol propane.

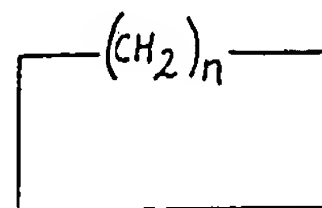
Particularly preferred alkylene oxides are ethylene oxide and propylene oxide, although other alkylene oxides such as 1,2- and 2,3-butylene oxides may be used. Conversion of the alkylene oxide condensates containing two hydroxyl groups into the diaminopolyalkyleneoxy compounds may be effected, for example, by the methods already described for conversion of polyalkylenediols into diaminopolyalkyleneoxy compounds.

Particularly preferred diaminopolyalkyleneoxy compounds are diamino poly(propylene oxide), diamino poly(hexamethylene oxide), diamino poly(octamethylene oxide) and diamino poly(decamethylene oxide). The diaminopolyalkyleneoxy compounds preferably have a molecular weight within the range 300 to 6000.

The aliphatic, cycloaliphatic or aromatic diamines which are optionally used as components in the condensates of the invention may be any aliphatic, cycloaliphatic or aromatic diamines including alkyl cycloaliphatic and alkyl aromatic diamines. Particularly preferred, however, are aliphatic diamines having the formula:—



in which n represents a positive integer of from 2 to 12. Hexamethylene diamine is particularly suitable. Other suitable aliphatic diamines include ethylene diamine, nonamethylene diamine, decamethylene diamine, dodecamethylene diamine and β - methylhexamethylene diamine. By cycloaliphatic diamines we mean diamines containing an alkylene ring structure:—



wherein n is from 5 to 16, two hydrogen atoms not on the same or adjacent carbon atoms being replaced by two amino groups to form the corresponding diamines. If aromatic diamines are used the amino groups should not be on adjacent atoms. Examples of suitable cycloaliphatic and aromatic diamines are 1,3- and 1,4-diaminocyclohexane, p-xylylene diamine, p-phenylene diamine and p-tolylene diamine. The diamine may be used in the form of a salt with the dicarboxylic acid.

It is preferred that the amount of dicarboxylic acid used in forming the condensate is the approximate stoichiometric equivalent of the amount of diamine used, whether diaminopolyalkyleneoxy compound or a mixture with another diamine.

The amount of diaminopolyalkyleneoxy compound used may vary within wide limits. We prefer, however, that the ratio of the weight of the diaminopolyalkyleneoxy compound to the combined weight of the amino acid or lactam and any other diamine which may be used should be within the range 10:90 to 95:5.

The condensates are conveniently prepared by mixing the components and heating them, for example at a temperature within the range 150° C. to 300° C. for about 30 minutes to 5 hours. Additives such as antioxidants, heat stabilisers, pigments and fillers which are stable under the polymerisation conditions may be included or these may be incorporated in the finished polymer.

In preparing the condensates there may be used instead of the dicarboxylic acid themselves certain derivatives of the dicarboxylic acids, for example the esters, especially the lower alkyl esters, and the halides of the said acids.

When an amino acid is used in place of a lactam it may be necessary to incorporate a 'flux', i.e. a substance which dissolves the components at the temperature of the reaction and which can be removed at the end of the reaction, e.g. by reducing the pressure and distilling out or by extraction with a solvent. An example of such a flux is o-phenylphenol. It may be desirable to carry out the condensation in an atmosphere of an inert gas such as nitrogen, or it may be desirable to carry out the condensation in the presence of a solvent such as water in a closed vessel under pressure.

The condensates of the invention are random polyamide condensates which are usually solids, often of a rubbery nature, some of which can be melt spun to highly extensible threads, others may be shaped by heating to foils, films or moulded articles. Depending on the amount of diaminopolyoxyalkylene compound used those polyamides which are fibre forming show varying degrees of tenacity and extensibility, for instance, if the propor-

tion of polyether is high the articles have high extensibility and low tenacity, and when the proportion is low they have a relatively high tenacity but reduced extensibility.

The invention is illustrated but not limited by the following Examples in which the parts and percentages are by weight:—

EXAMPLE 1

Diaminopolypropylene glycol mol.wt 2060, 50 parts by weight, adipic acid 3.3 parts and caprolactam 50 parts, are heated at 224° C. with stirring under a stream of nitrogen for 4½ hours. At the end of this period the pressure is lowered to 15 mm. over 1 hour and held at 15 mm. for 10 minutes. The product is cooled, minced, extracted with boiling water and then dried. The polymer has a molecular weight of 9000 as determined by analysis of end groups. It can be extruded from a spinneret at 220° C. to form high elastic threads.

EXAMPLE 2

70 Parts α,ω - diaminopolytetramethylene oxide of molecular weight 3000, 3.3 parts of adipic acid and 30 parts of caprolactam are treated as in Example 1. A translucent tough rubbery product mol.wt. 24000 is obtained which melt spins at 220° C. into strong elastic fibres. After drawing 2× these have reversible extensibilities of 600%.

EXAMPLE 3

70 Parts α,ω - diaminopolyoxyethylene of molecular weight 1464, 30 parts of caprolactam and 7.0 parts of adipic acid are stirred together at 259° C. under a stream of oxygen-free nitrogen for 2 hours, 20 minutes. The product when cooled to room temperature is a pale yellow, translucent, rubbery solid soluble in water.

EXAMPLE 4

50 Parts of α,ω - diaminopolyoxyethylene of molecular weight 1464, 50 parts of caprolactam and 5.0 parts of adipic acid are heated under similar conditions to those of Example 3 at 259° C. for 1 hour, 45 minutes. The cooled product is an almost colourless opaque solid, rubbery and less soluble in water than that of Example 3.

EXAMPLE 5

70 Parts of α,ω - diaminopolyoxyethylene of molecular weight 1464, 30 parts of caprolactam, 7.0 parts of adipic acid and 50 parts of water are heated in an autoclave for 1 hour at 230° C. the pressure being maintained at 250 lb./sq.in. (gauge) by bleeding off water vapour. The temperature is then raised to 240° C. over ½ hour and the pressure is reduced to atmospheric. The autoclave is then heated at 250° C. for 1 hour at atmospheric pressure. The polymer is similar in properties to that in Example 3.

EXAMPLE 6

25 Parts of α,ω - diaminopolyoxyethylene of molecular weight 1532, 2.4 parts of adipic acid, 15 parts of caprolactam and 10 parts of the salt of hexamethylene diamine and adipic acid are stirred together at 259° C. under a stream of oxygen-free nitrogen for 3½ hours. The product when cooled to room temperature is a pale yellow, translucent, rubbery solid.

EXAMPLE 7

40 Parts of α,ω - diaminopolyoxyethylene of molecular weight 1540, 4.0 parts of adipic acid, 24 parts of caprolactam and 36 parts of the salt of hexamethylene diamine and adipic acid are stirred together at 259° C. under a stream of oxygen-free nitrogen for 1½ hour. The product is pale yellow in colour, rubbery, melt spins, and is soluble in a mixture of water and ethyl alcohol.

EXAMPLE 8

The above example is repeated using 30 parts of α,ω - diaminopolyoxyethylene of molecular weight 1454, 3.0 parts of adipic acid, 28 parts of caprolactam and 42 parts of the salt of hexamethylene diamine and adipic acid. The product is pale yellow, translucent, rubbery and dissolves in aqueous ethyl alcohol.

EXAMPLE 9

60 Parts of α,ω - diaminopolyoxyethylene of molecular weight 1540, 40 parts of caprolactam and 5.7 parts of adipic acid are stirred together at 259° C. under a stream of oxygen-free nitrogen for 2 hours. The product is discharged into a well-stirred mixture of 900 parts of water and 400 parts of isopropanol, previously heated to 60° C. A clear solution is obtained, setting to a gel on cooling.

EXAMPLE 10

25 Parts of an aminomethyl tetrahydropyran - terminated polyoxyethylene (prepared from polyoxyethylene glycol of molecular weight 1540 by reaction with aminomethyl dihydropyran), 25 parts of caprolactam and 2.6 parts of adipic acid are reacted together at 190° C. under a stream of oxygen-free nitrogen for 3½ hours, and then at 190° C./15 mm. pressure for 1½ hours to give a hard, somewhat brittle polymer.

EXAMPLE 11

25 parts of α,ω - diaminopolyoxyethylene of molecular weight 1532, 2.4 parts of adipic acid, 6.5 parts of caprolactam, 9.0 parts of the salt of hexamethylenediamine and adipic acid and 9.5 parts of the salt of hexamethylene diamine and sebacic acid are stirred together at 259° C. under a stream of oxygen-free nitrogen for 2½ hours. The product on cooling to room temperature is a pale yellow rubbery solid.

EXAMPLE 12

25 Parts of α,ω - diaminopolyoxyethylene of molecular weight 1532, 3.3 parts of dimethyl terephthalate, 25 parts of caprolactam and 1 part of water are stirred together at 259° C. under a stream of oxygen-free nitrogen for 2 hours. The product on cooling to room temperature is a pale yellow rubbery solid.

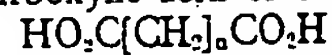
EXAMPLE 13

25 Parts of a diamine prepared by reacting a condensate of octadecylamine and 18 moles of ethylene oxide successively with thionyl chloride and ammonia, 3.1 parts of adipic acid and 25 parts of caprolactam are stirred together at 259° C. under a stream of oxygen-free nitrogen for 2 hours. The product on cooling to room temperature was a tough brown rubbery solid.

WHAT WE CLAIM IS:—

1. Condensation products of a dicarboxylic acid with a mixture of a diaminopolyalkyleneoxy compound which has a molecular weight within the range 300 to 6,000 and an aliphatic, cycloaliphatic or alkyl cycloaliphatic amino acid and/or lactam, and optionally an aliphatic, cycloaliphatic or aromatic diamine.

2. Condensation products as claimed in Claim 1 in which the dicarboxylic acid is an aliphatic dicarboxylic acid of the formula:—



in which n represents zero or a positive integer from 1 to 10.

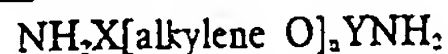
3. Condensation products as claimed in claim 2 in which the dicarboxylic acid is adipic acid.

4. Condensation products as claimed in any of claims 1 to 3 in which the diaminopolyalkyleneoxy compound is a compound of the formula:—



in which X represents a direct link, Y represents an alkylene group and n is a positive integer.

5. Condensation products as claimed in any of claims 1 to 3 in which the diaminopolyalkyleneoxy compound is a compound of the formula:—



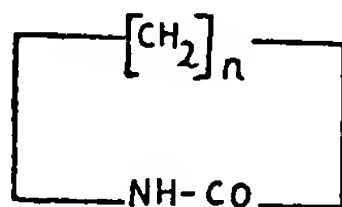
in which X represents a 2 - methylenetetrahydropyran - 6 - yloxy group, Y represents a 2 - methylene tetrahydropyran - 6 - yl group and n is a positive integer, and in which the two amino groups are attached to the 2-methylene groups of X and Y respectively.

6. Condensation products as claimed in any of claims 1 to 4 in which the diaminopolyalkyleneoxy compound is a diamino poly(propylene oxide).

7. Condensation products as claimed in any of claims 1 to 6 in which the amino acid or lactam is an ω -amino aliphatic carboxylic acid of the formula:—



or a lactam of the formula:—



in which n is a positive integer from 5 to 11 or a mixture of a said acid and lactam.

8. Condensation products as claimed in claim 7 in which the amino acid or lactam is caprolactam.

9. Condensation products as claimed in any of claims 1 to 8 in which an aliphatic diamine of the formula:—



in which n represents a positive integer of from 2 to 12 is used as one of the components of the condensate.

10. Condensation products as claimed in claim 9 in which the aliphatic diamine is hexamethylene diamine.

11. Condensation products as claimed in any of claims 1 to 10 in which the amount of dicarboxylic acid used in forming the condensate is the approximate stoichiometric equivalent of the amount of diamine used, whether diaminopolyalkyleneoxy compound or a mixture thereof with another diamine.

12. Condensation products as claimed in any of claims 1 to 11 in which the ratio of the weight of the diaminopolyalkyleneoxy compound to the combined weight of the amino acid or lactam and any other diamine

which may be used lies within the range 10:90 to 95:5.

13. Condensation products substantially as herein particularly described with reference to the Examples.

14. A process for the manufacture of condensation products as claimed in any of claims 1 to 13 which comprises mixing a dicarboxylic acid, a diaminopolyalkyleneoxy compound and an aliphatic, cycloaliphatic or alkyl cycloaliphatic amino acid and/or lactam and optionally an aliphatic, cycloaliphatic or aromatic diamine and heating the mixture.

15. A process as claimed in claim 14 in which the diamine is used in the form of a salt with the dicarboxylic acid.

16. A process as claimed in either of claims 14 or 15 in which the mixture is heated at a temperature within the range 150° C. to 300° C. for from 30 minutes to 5 hours.

17. A process as claimed in any of claims 14 to 16 in which the condensation is carried out in an atmosphere of an inert gas.

18. A process as claimed in any of claims 14 to 17 in which the condensation is carried out in the presence of water in a closed vessel under pressure.

19. A process for the manufacture of condensation products substantially as herein particularly described with reference to the Examples.

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Agent for the Applicants.

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